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DIFFUSION BEHAVIOR OF SUPERSATURATED BINARY SOLUTIONS

By

Jacob Mazur and Turner Alfrey, Jr.

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Jacob Mazur and Turner Alfrey, Jr.
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Accorded an A. Cressy Morrison Award in Natural Science in 1959
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IFFUSION BEHAVIOR OF SUPERSATURATED BINARY SOLUTIONS

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PART I

The nonideality of binary mixtures may be attributed to a number of tors, including differences in size and shape. We restrict our discus- n to the nonideality arising entirely from the unequal intermolecular ces between the molecules. We assume a lattice filled with a mixture 2 species of spherical molecules, *A* and *B*, having identical diameters different chemical constitutions. The coordination number of the tice will be designated as z. The deviation of the binary mixture from ality is determined by the average potential energy of an *A*-*B* pair,

$$\Delta\epsilon = \epsilon_{AB} - \frac{\epsilon_{AA} + \epsilon_{BB}}{2}$$

ere ϵ_{AA} is the energy of association of an *A*-*A* pair, ϵ_{BB} is the energy association of a *B*-*B* pair, and ϵ_{AB} is the energy of association of an B pair (ϵ_{AA}, ϵ_{BB}, and ϵ_{AB} are negative in sign). Negative values of mean that the mixing is exothermic (strong affinity of *A* molecules for nolecules). Positive values of $\Delta\epsilon$ mean that the mixing is endothermic. $\Delta\epsilon$ is sufficiently positive, limited miscibility results.

The statistical thermodynamics of this model have been analyzed by ny investigators.* Even the crudest treatment (usually designated as eroth-order'' approximation) leads to a reasonable qualitative descrip- n of the behavior of such mixtures in spite of a nonzero $\Delta\epsilon$ and the sumption of random mixing.

The free energy versus composition curve (with the assumption of dom mixing) has, for sufficiently large positive values of $\Delta\epsilon$, 2 minima d a central maximum (FIGURE 1). Any homogeneous solution having a nposition between n_1 and n_2 (the 2 minima) will be unstable relative to nixture of 2 separate phases having the compositions n_1 and n_2. If a nogeneous solution of intermediate composition n ($n_1 < n < n_2$) is ned, the free-energy curve requires that it should separate into 2 such ses. However, there are 2 different kinds of unstable solutions: tastable solutions and absolutely unstable solutions. In metastable utions $(\partial^2 F/\partial n^2)_{T,P} > 0$ (n is the mole fraction of molecules *A*). erefore, minor fluctuations in concentration tend to increase the free rgy of the system. The fluctuation in concentration tends to be wiped

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*For an up-to-date review of the problem of the stability of binary mixtures, see ogine.[1]

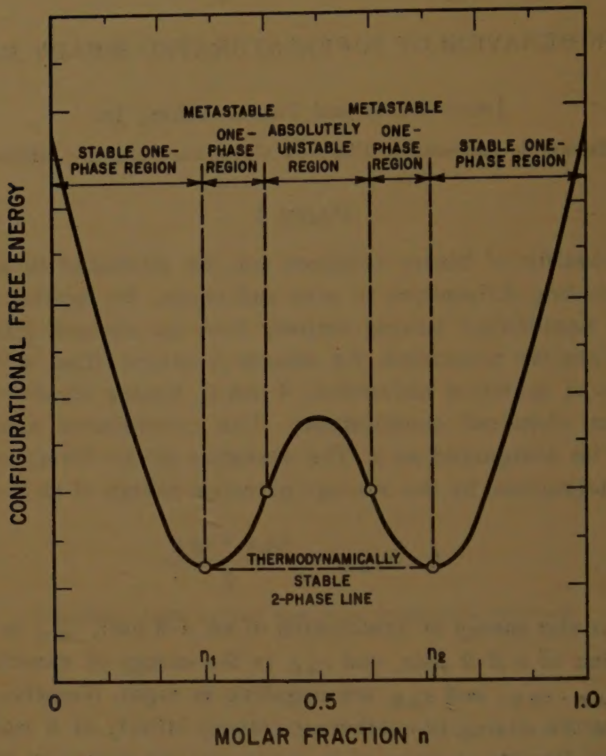

FIGURE 1. Configurational free energy of binary mixtures.

out, and the solution, in the absence of seeding, may persist for a ve long time.* In the regions where $(\partial^2 F/\partial n^2)_{T,P} < 0$, the F versus n curv is concave downward. Hence, any minor fluctuation in concentration lead to a decrease in free energy; therefore, such a solution is absolute unstable with regard to concentration fluctuations, and it will split spo taneously into 2 different phases.

The behavior of a solution in the absolutely unstable region can described in terms of a "negative diffusion coefficient," since a conce tration gradient will cause diffusion up the gradient, rather than down i and thus accentuate the difference in concentration.

We propose to reexamine the lattice model in the statistical therm dynamic treatment described above, to introduce an elementary diffusio process (consisting of molecular interchanges), and to deduce from t expanded model an approximate expression for the diffusion coefficie as a function of concentration.

---

*The possibility of a phase separation in a metastable solution in the absence seed (the so-called heterophase fluctuation) is discussed by Frenkel.[2]

Toward this end we assume the existence of a 1-dimensional concen- ation gradient in the positive x direction. In any layer of the lattice riented normal to the x direction we assume a constant composition and random arrangement of the 2 types of molecules. Furthermore, we as- ume that $n(x)$ is a continuous function with continuous derivatives. (The ase with discontinuities in $n(x)$, that is, when the equilibrium configura- ion involves sharp phase boundaries, is discussed below.)

Let us now consider a particular molecular pair interchange in a binary attice. An A-B pair in arrangement will be "rotated" to the interchanged rrangement II with a certain rate that will depend upon the activation nergy $E_{\mathrm{I}\to\mathrm{II}}$ for the process. The number of A-B interchanges of this articular variety occurring per second across a given plane of the lattice ill be proportional to: (The number of sites per layer) · (the probability iat a given pair of sites accommodates an A-B pair) · (the probability iat the "atmosphere" of neighbors is the particular one) · $(e^{\Delta S\ddagger/k})$ · $e^{-E_{\mathrm{I}\to\mathrm{II}}/kT}$). The number of transitions of the precisely reverse form I→I) will be given by a similar expression: (sites/layer) · (probability iat a given pair of sites accommodates a B-A pair) · (the probability that ie "atmosphere" of neighbors is the particular one) · $(e^{\Delta S^{\dagger}/k})$ · $^{-E_{\mathrm{II}\to\mathrm{I}}/kT}$. $\Delta S^{\dagger}$ is the entropy of activation of the molecular interchange.

The net flux of molecules A to the right, across the boundary, resulting om the interchanges of these 2 detailed types is equal to the difference etween the 2 terms above. It is assumed that $\Delta S^{\ddagger}$ is the same for all etailed molecular interchanges. Although the absolute values of $E_{\mathrm{I}\to\mathrm{II}}$ nd $E_{\mathrm{II}\to\mathrm{I}}$ are indeterminate, the difference between them is fixed by m, ie net change in the number of A-B "bonds" between the 2 states IGURE 2).

We now choose a new reference point in such a way that

$$e^{-(E_{\mathrm{I}\to\mathrm{II}})/kT} = e^{-E'/kT} \cdot e^{-m\Delta\epsilon/2kT}$$

ıd

$$e^{-(E_{\mathrm{II}\to\mathrm{I}})/kT} = e^{-E'/kT} \cdot e^{m\Delta\epsilon/2kT}$$

hus, since we are interested only in the net flux up or down the concen- ation gradient, we may factor out not only the indeterminate value of $^{\Delta s\ddagger/k}$ but also the indeterminate part of each activation energy $e^{-E'/kT}$, s well as the number of sites per layer, into 1 comprehensive indeter- inate constant, K.

In the absence of a concentration gradient, the above pair of specific ementary interchanges will lead to a net flux (because of the asymmetry the atmosphere), but this will be just counterbalanced by a net flux in e opposite direction by interchanges of a similar type with reversed

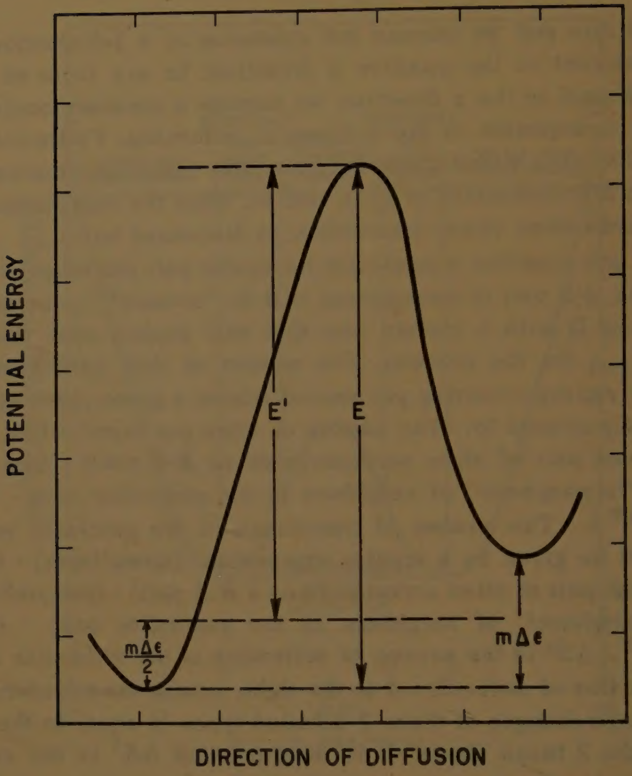

FIGURE 2. Change in energy for a typical molecular interchange.

atmospheres. This offsetting will lead to an over-all net flux of zero. I the presence of a concentration gradient, the over-all net flux is not zero In some concentration ranges the flux per unit gradient is positive (o cogradient); in some it is negative (or contragradient). The dependence o the net flux on the concentration will be determined next.

PART II

Let us consider an "atmosphere" of N_A molecules A, N-N_A molecule B, which are distributed among N sites. Let these sites be located alon 4 equivalent lines perpendicular to the x axis, as in FIGURE 3.

Let the coordinates of the neighbors be 0, Δx, 2 Δx, and 3 Δx. W again assume that the molecules A and B are randomly arranged along th lines perpendicular to the x axis. Therefore, the probability that a mole cule A will occupy 1 of the sites along the line $x = 0$ is simply n_A, o for brevity, n. For the molecule B, this probability is $1 - n$. Owing to th concentration gradient along the x axis, this probability will be altere as we move along it. Thus, along the line with $x = \Delta x$, this probability i

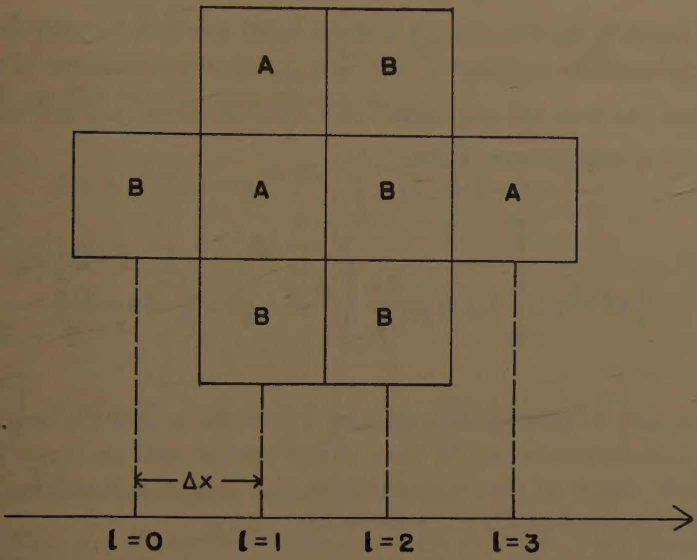

FIGURE 3. Location of *N* sites *(see text)*.

For molecules *A:*

$$n + \Delta x \frac{\partial n}{\partial x}$$

For molecules *B:*

$$1 - n - \Delta x \frac{\partial n}{\partial x}$$

Let there be a_0 "atmosphere" sites along the line $x = 0, a_1$ sites along line $x = \Delta x$, and other such sites. Obviously, $\sum_{\ell=0}^{\ell=3} a = N$. Let there be molecules A along $x = 0$, j_1 molecules A along $x = \Delta x$, and so on. en the probability C of having an atmosphere of specific structure is:

$$C = \prod_{\ell=0}^{\ell=3} \left[n + \ell \Delta x \frac{\partial n}{\partial x} \right]^{j_\ell} \left[1 - n - \ell \Delta x \frac{\partial n}{\partial x} \right]^{a_\ell - j_\ell}$$

$$\sum_{\ell=0}^{\ell=3} j_\ell = N_A \quad ; \quad \sum_{\ell=0}^{\ell=3} (a_\ell - j_\ell) = N_B \qquad \text{(II,1)}$$

In our diagram $a_0 = a_3 = 1,\ a_1 = a_2 = 2;\ j_0 = j_2 = 0;\ j_1 = j_3 = 1.$

This "probability product" C can be simplified if all powers of Δx - higher than the first are neglected. The simplification is justified, sin $\Delta x \frac{\partial n}{\partial x} \ll n$, everywhere. Then,

$$C = n^{N_A}(1-n)^{N-N_A}\left[1 + \Delta x \frac{\partial n}{\partial x}\left(\frac{\sum_{\ell=0}^{3} \ell j_\ell}{} - \frac{\sum_{\ell=0}^{3} \ell (a_\ell - j_\ell)}{1-n}\right)\right]$$

(II,

It is necessary to multiply this term by a probability that the central pa of sites accommodates an AB pair. Since the AB pair is located in th geometrical center of the atmosphere on the lines $\ell = 1$ and $\ell = 2$, th probability, denoted as D_{AB}, is given by

$$D_{AB} = \left(n + \Delta x \frac{\partial n}{\partial x}\right)\left(1 - n - 2\,\Delta x \frac{\partial n}{\partial x}\right) \qquad \text{(II,}$$

Multiplying C and D_{AB} and neglecting again the second powers of $\Delta x \frac{\partial}{\partial}$ we obtain:

(Probability of an AB pair) · (probability of the particular atmosphere described by $j_0, \ldots\ldots, j_3$) =

$$n^{N_A}(1-n)^{N-N_A}\left\{n(1-n) + \Delta x \frac{\partial n}{\partial x}\left[(1-n)\sum_{\ell=0}^{3} \ell j_\ell - n\sum_{\ell=0}^{3} \ell (a_\ell - j_\ell) - (3n-1)\right]\right\}$$

(II,

Similarly, for the reverse configuration we obtain

$$CD_{BA} = n^{N_A}(1-n)^{N-N_A}\left\{n(1-n) + \Delta x \frac{\partial n}{\partial x}\left[(1-n)\sum_{\ell=0}^{3} \ell j_\ell - n\sum_{\ell=0}^{3} (\ell a_\ell - j_\ell) - (3n-2)\right]\right\}$$

(II,

The net flux of A to the right for this particular pair of reverse inter-anges is proportional to $CD_{AB}\ e^{-E_{I\to II}/kT} - CD_{BA}\ e^{-E_{II\to I}/kT}$. There-e, the net flux for this interchange is

$$\Phi = Kn^{N_A}(1-n)^{N-N_A}\left\{n(1-n) + \Delta x\,\frac{\partial x}{\partial n}\right.$$

$$\left[(1-n)\sum_{\ell=0}^{3}\ell j_\ell - n\sum_{\ell=0}^{3}\ell\,(a_\ell - j_\ell) - (3n-1)\right] \tag{II,6}$$

$$\left.\left[e^{-E_{I\to II}/kT} - e^{-E_{II\to I}/kT}\right] - \Delta x\,\frac{\partial n}{\partial x}\,e^{-E_{II\to I}/kT}\right\}$$

ere K is an indeterminate constant.

Since $E_{I\to II} = E' + \dfrac{m\Delta\epsilon}{2}$, $E_{II\to I} = E' - \dfrac{m\Delta\epsilon}{2}$, and since E' is sumed to be independent of the structure of the atmosphere, the net x of A to the right for the particular pair of interchanges is

$$\Phi = Kn^{N_A}(1-n)^{N-N_A}\left\{n(1-n) + \Delta x\,\frac{\partial n}{\partial x}\right.$$

$$\left[(1-n)\sum_{\ell=0}^{3}\ell j_\ell - n\sum_{\ell=0}^{3}(a_\ell - j_\ell) - (3n-1)\right] \tag{II,7}$$

$$\left.2\sinh\frac{m\Delta\epsilon}{2kT} - \Delta x\,\frac{\partial n}{\partial x}\,e^{m\Delta\epsilon/2kT}\right\}$$

As the next step, we shall find the connection between m, the net ange in number of AB "bonds," and the arrangement of the molecules the particular atmosphere. The quantity m is independent of the way e molecules distribute between the sites with $\ell = 0$ and $\ell = 1$, and sim-rly, between the sites with $\ell = 2$ and $\ell = 3$. However, m depends upon e way the molecules distribute between the 2 halves of the atmosphere. Let there be i molecules A at the left side of the atmosphere, and $-i$ at the right side of the atmosphere, with $i = j_0 + j_1$; $N_A - i = j_2 + j_3$. erefore, $m = 2(N_A - 2i)$.

The total flux resulting from all possible interchanges AB and BA is sum of EQUATION II,7 over all possible arrangements of the mole-les. The derivation of the total flux from EQUATION II,7 is shown in

APPENDIX I. The equation for the total flux is solved explicitly for following cases:

Case I: $z=4;\ a_0=a_3=1,\ a_1=a_2=2$

Case II: $z=6;\ a_0=a_3=1,\ a_1=a_2=4$

Case III: $z=8;\ a_0=a_3=1,\ a_1=a_2=6$

The various terms in the equations for the total flux are arranged in following way:

$$\text{Total flux} = K' \left[\sum_{p=0}^{z-1} A_p(n) \sinh\left(\frac{p\Delta\epsilon}{kT}\right) - B_p(n) \cosh\left(p\frac{\Delta\epsilon}{kT}\right.\right.$$

(II

where $A_p(n)$ and $B_p(n)$ represent polynomials in n of the order $2(z -$ Since $A_p(n)$ and $B_p(n)$ are always positive, the first term of the rig hand side of EQUATION II,8 represents the contribution of the "cont gradient" flow, while the last term represents the contribution of "cogradient" flow toward the total flux, when $\Delta\epsilon > 0$. When $\Delta\epsilon < 0$, b terms will be cogradient, and we have a case in which the net free ene of activation will "reinforce" the diffusion flow from higher to lo concentrations.

It will be worthwhile to show the solution of EQUATION II,8 wh $\Delta\epsilon = 0$, as a check of our derivation. In this case,

$$\text{Total flux} = -K' \sum_{p=0}^{z-1} B_p(n) = -K' \sum_{p=0}^{z-1} \binom{\frac{N}{2}}{\frac{N_A}{2}} {}^{A}(1-n)^{N-N_A} =$$

(II

$$K' \sum_{t=0}^{N/2} \binom{\frac{N}{2}}{t} n^t (1-n)^{\frac{N}{2}-t} = -K'$$

by binomial expansion.

A further comment should be made about the indeterminate constant This constant includes not only $e^{-E'/kT}$, but the concentration gradie $\Delta x \dfrac{\partial n}{\partial x}$ as well. In other words, the net flux is taken now as per u gradient.

The results of numerical computations are given in FIGURES 4, 5, a 6, in which the net flux (expressed as $-D/D_0$) is plotted as a function n for several values of $\Delta\epsilon/kT$. We notice that there exists a critic value of $\Delta\epsilon$ below which the flux is always cogradient. This value

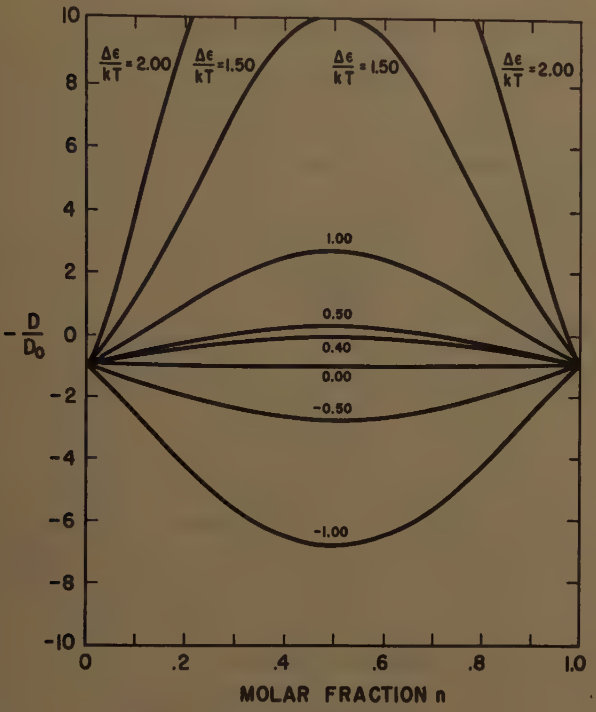

Figure 4. The dependence of the net flux on concentration for $z = 4$.

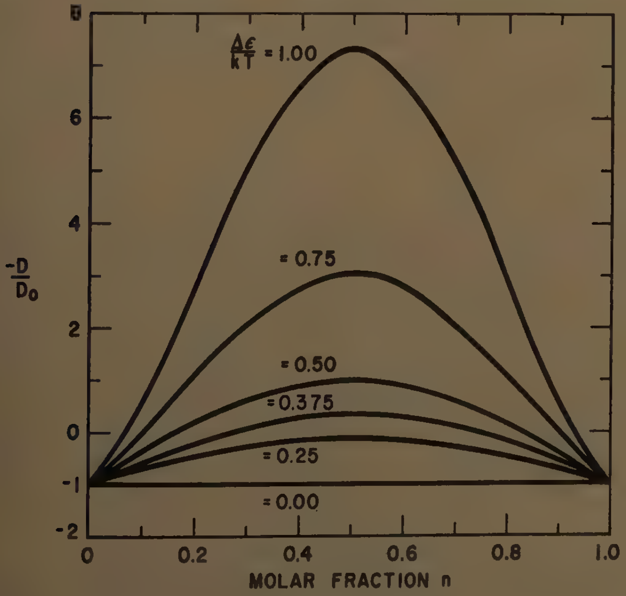

Figure 5. The dependence of the net flux on concentration for $z = 6$.

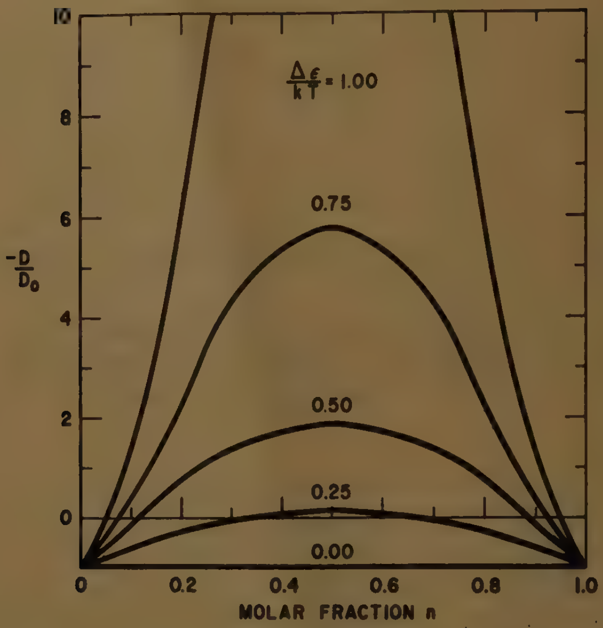

FIGURE 6. The dependence of the net flux on concentration for $z = 8$.

$\Delta\epsilon$ (= $\Delta\epsilon^*$) depends not only upon the coordination number z but al upon the way the sites are arranged along the diffusion coordinate (other words upon a). The dependence of $\Delta\epsilon^*$ (and of D/D_0) on the geo etry of the lattice arrangements is in striking contrast to the implicatio of the thermodynamic model, where D/D_0 and $\Delta\epsilon^*$ depend only on z for given value of $\Delta\epsilon/kT$.

PART III

The thermodynamic theory of regular solutions enables us to constru the excess free-energy curve as a function of concentration for conce trated binary solutions. As was pointed out in PART I, these free-energ curves in some cases possess 2 "inflection points." The concentratio enclosed by these inflection points (symmetrically arranged arou $n = 0.5$) correspond to an absolutely unstable region that can be describe by negative diffusion coefficients (for example, the parts of FIGURES 5, and 6, where the total net flux is greater than zero). These inflectio points are defined by

$$\frac{d^2 F}{dn^2} = 0 \qquad \text{(III,}$$

(at given T and p)

ese points should correspond to the zero net flux. We shall therefore
mpare our conditions for zero flux with the solutions of EQUATION
,1. This is done as follows.

The statistical thermodynamic theory of regular solutions, based upon
"zeroth-order" approximation, gives the following equation for the
cess free energy of binary solution (in terms of mole fraction n);

$$\frac{F}{{}_A^* + N_B^*} = -kT\left[n \log n + (1-n)\log(1-n) + n(1-n)\frac{w_{AB}}{kT}\right] + F' \tag{III,2}$$

N_A^* and N_B^* are the number of molecules of the species A and B. F' in-
udes all terms that enter into the free energy, but that are independent
n. The quantity w_{AB} is one half of the total increase of potential
ergy of molecular interchange. From EQUATIONS III,1 and III,2 we
ve as a condition for zero net flux

$$\frac{w_{AB}}{kT} = \frac{1}{2n(1-n)} \tag{III,3}$$

,

$$\frac{\Delta\epsilon_{AB}}{kT} = \frac{1}{2zn(1-n)} \tag{III,4}$$

FIGURE 7 shows the solution of EQUATION III,4 for $z = 4$, 6, and 8,
here n is given as a function of $\Delta\epsilon$. In the same plot the conditions for
ro flux, as obtained from FIGURES 4, 5, and 6, are plotted in similar
shion. We notice good qualitative agreement between the results based
our kinetic model and the thermodynamic model. We also notice that
e conditions for zero flux based on the kinetic model show a stronger
pendence on z than the thermodynamic model. That is, in the kinetic
odel increasing z will shift the values of n for which the total flux is
ro toward terminal points more rapidly than in the case of the thermo-
namic model. This difference is not surprising since, as stated before,
e equation for flux based on the kinetic model is a polynomial in n of the
der of $2(z-1)$, instead of the second order in n, as in the case of the
ermodynamic model. Also, in our particular models we assumed that
$= 1$. Should we reshuffle the neighbors so that a_0 no longer is unity,
e obtain a different flux-versus-concentration curve. Therefore, we would
tain different results for the conditions of zero flux.

We next derive an equation for the net flux using an expression ob-
ined by Stearn *et al.*[3] and the thermodynamic equation for excess free
ergy of randomly mixed concentrated binary solutions. These authors

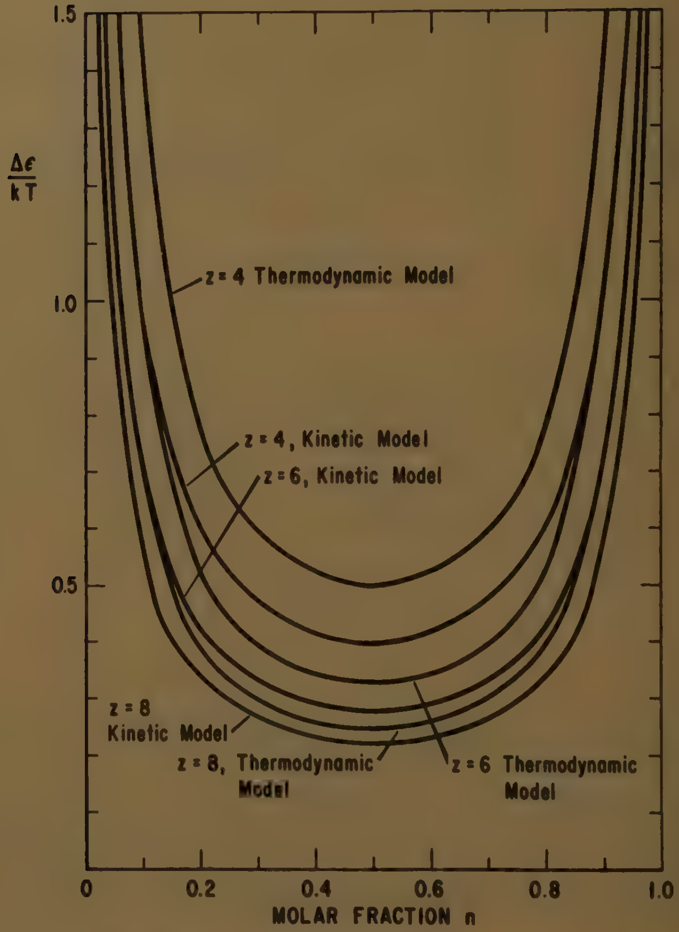

FIGURE 7. Conditions for the zero net flux; comparison of the kinetic the thermodynamic models.

derived a simple equation in differential form for the diffusion coefficie in concentrated solutions. They base their result upon the assumpti that it is the activity, and not the concentration, that is the driving for in diffusion. The expression for the diffusion coefficient is given these authors as follows:

$$\frac{D}{D_0} = \frac{d \log a_A}{d \log n} \qquad \text{(III,}$$

where D is the diffusion coefficient of the concentrated solution, D_0 the diffusion coefficient of an ideal solution, and a_A is the activity the species A. D/D_0 is what we calculated as the term proportional the net flux.

In order to compare our results with EQUATION III,1 we solve EQUA- ION III,5 for our thermodynamic model. This is done as follows:

The activity of molecules A is defined as

$$kT \log a_A = \mu_A - \mu_A^0 \qquad \text{(III,6)}$$

here $\mu_A - \mu_A^0$ is the chemical potential of the solution with respect to arbitrarily chosen standard solution whose chemical potential is μ_A^0.

rom

$$\mu_A = \left(\frac{\partial F}{\partial N_A^*}\right)_{N_B^*}$$

e obtain

$$\frac{d \log a_A}{d \log n} \left(\equiv \frac{D}{D_0}\right) = \frac{N_A^*}{N_B^*} (N_A^* + N_B^*) \left[\frac{N_B^*}{N_A^* (N_A^* + N_B^*)} - \frac{2 w_{AB} N_B^*}{(N_A^* + N_B^*)^2} \left(1 - \frac{N_B^*}{N_A^* + N_B^*}\right) \right]$$

, simply

$$\frac{D}{D_0} = 1 - 2n(1-n) \frac{z \Delta\epsilon}{kT} \qquad \text{(III,7)}$$

We observe that the net flux is a quadratic function of n irrespective of while, in our kinetic treatment, D/D_0 is a polynomial in n of the order $2(z-1)$.

PART IV

We assume now that we have 2 homogeneous binary solutions, of differ- nt concentrations, in contact. This means that $n(x)$ is a discontinuous nction of x of the form shown in FIGURE 8. The concentration of mole- les of the species A to the left of the point of discontinuity $x = x^*$ is qual to $(n-d)$, while the concentration of the species A to the right of e point of discontinuity is equal to $(n+d)$.

Before proceeding with the derivation of the equation for the flux based pon FIGURE 8, let us pause and consider the various possibilities that r model implies.

The model allows each of the 2 phases that are in contact to be either a stable state, in a metastable state, or in an absolutely unstable ate.

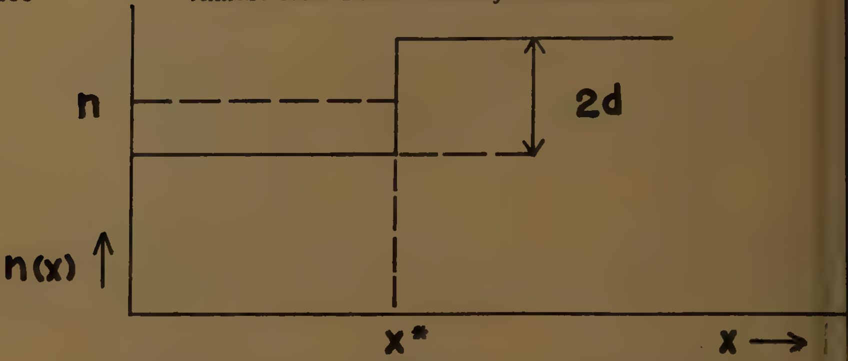

FIGURE 8. $n(x)$ as a discontinuous function of x (see text).

Let the molar free energy of phase 1 be F_1 and the molar free energy phase 2 be F_2. Let n_1 be the molar fraction of component A in phase and n_2 be the molar fraction of component A in phase 2. Then the cond tion for the system to be in equilibrium with regard to the exchange material across the boundary is

$$\frac{dF_1}{dn_1} = \frac{dF_2}{dn_2}$$

At constant temperature and pressure,

$$dF_1 = (\mu_1^A - \mu_1^B)\, dn_1$$

and

$$dF_2 = (\mu_2^A - \mu_2^B)\, dn_2$$

Therefore, the condition for the binary solutions to form a stable or metastable state is

$$\mu_1^A - \mu_1^B = \mu_2^A - \mu_2^B$$

This is a necessary but not sufficient condition for an "equilibrium." W must still introduce limitations on each of the 2 solutions separately t prevent them from breaking spontaneously into 2 phases, even without mutual contact. At constant temperature and pressure, we require that

$$\frac{d^2F_1}{dn_1^{\,2}} > 0 \text{ and } \frac{d^2F_2}{dn_2^{\,2}} > 0$$

If phases 1 and 2 are both stable, then these conditions are met if an only if

$$\mu_1^A = \mu_2^A \quad ; \quad \mu_1^B = \mu_2^B$$

hat is, the concentrations of component A will correspond to the 2 min-ma indicated by n_1 and n_2 (FIGURE 1). However, if one of the 2 phases s in a metastable state, the entire system can form a metastable state ince, generally, $\mu_1^A \ddagger \mu_2^A$.

Our task will be to investigate, with the aid of the kinetic model, what recisely are the conditions for the zero flux and how they compare with esults of thermodynamic models. This is done again by employing a inetic model for the derivation of the equation for the total net flux of omponent A across the boundary. In many details the derivation of an xpression for the total flux will be a repetition of our first problem.

As before, we consider a molecular-pair interchange in a binary lattice FIGURE 9). However, the concentration of molecules to the left of the oundary is constant, and so is the concentration of the molecules to the ight of the boundary (or point of discontinuity). The number of A-B inter-hanges will be given by: (The number of sites per layer) · (the probabil-ty that a given pair of sites accommodates an A-B pair) · (the probability hat the atmosphere of neighbors is the particular one) · ($e^{\Delta s^\ddagger/k}$) · $e^{-E_{\mathrm{I}\to\mathrm{II}}/kT}$). A similar expression will be obtained for the number of recisely reverse interchanges B-A, except that the second term denotes he probability that a given pair of sites accommodates a B-A pair, and he last term will be $e^{-E_{\mathrm{II}\to\mathrm{I}}/kT}$. The net flux of A to the right resulting rom this pair of interchanges is the difference between these 2 terms.

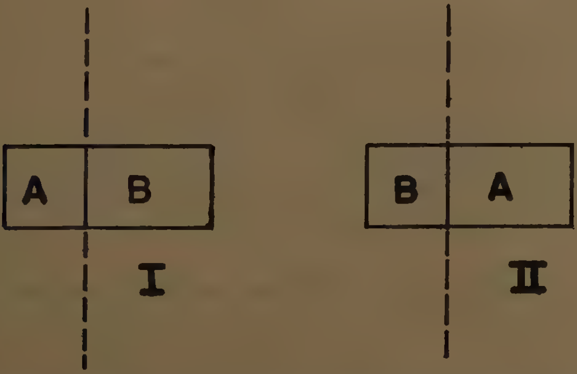

FIGURE 9. Molecular pair interchange in a binary lattice.

We shall now proceed to derive the individual terms in the expression or the net flux of A and then, by summing this expression over all pos-sible arrangements of molecules in the surroundings or atmospheres, we hall obtain an expression for the net flux of A to the right of the bound-ry point $x = x^*$.

The probability that the given pair of sites accommodates molecular pair AB is proportional to:

$$D_{AB} = (n-d)\,(1-n-d) \qquad \text{(IV,1}$$

The probability that the atmosphere of neighbors has a given arrangemen (described by N_A and i, where N_A is the number of molecules A in th atmosphere, while i is the number of molecules A in the atmosphere t the left of the point of the discontinuity x^*) is

$$C = (n-d)^i\,(1-n+d)^{N/2-i}\,(n+d)^{N_A-i}\,(1-n-d)^{N/2-N_A+i}$$

The net flux from the pair of interchanges is proportional to the ter

$$C\;[D_{AB}\,e^{-E_{I\to II}/kT} - D_{BA}\,e^{-E_{II\to I}/kT}] \qquad \text{(IV,2}$$

where D_{AB} is given by EQUATION IV,1 and

$$D_{BA} = (1-n+d)\,(n+d) \qquad \text{(IV,3}$$

Since, according to the adopted model for the energy of activation of th transition from state I to state II,

$$\begin{aligned} e^{-E_{I\to II}/kT} &= e^{-E'/kT}\,e^{-m\Delta\epsilon/2kT} \\ e^{-E_{II\to I}/kT} &= e^{-E'/kT}\,e^{m\Delta\epsilon/2kT} \end{aligned} \qquad \text{(IV,4}$$

we obtain the following expression for the net flux per molecular inter- change

$$\Phi = 2K\cdot\Big[(n-d)^i\,(1-n+d)^{N/2-i}\,(n+d)^{N_A-i}\,(1-n-d)^{N/2-N_A+i}\Big]$$

$$\Big[(n-n^2+d^2)\sinh\frac{m\Delta\epsilon}{2\,kT} - d\cdot\cosh\frac{m\Delta\epsilon}{2\,kT}\Big] \qquad \text{(IV,5}$$

The total flux will be obtained by summing EQUATION IV,5 over al possible arrangements of the molecules in the atmosphere with the fol- lowing restrictions imposed on i and N_A:

$$0 \leqslant i \leqslant N_A\,; \qquad 0 \leqslant N_A \leqslant N$$

e total flux is now

$$\text{Total flux} = 2K\left[(1-n)^2 - d^2\right]^{N/2} \sum_{N_A=0}^{N} \sum_{i=0}^{N_A} \binom{\frac{N}{2}}{i}\binom{\frac{N}{2}}{N_A-i} \left(\frac{n-d}{1-n+d}\right)^{i} \left(\frac{n+d}{1-n-d}\right)^{N_A-i} \left\{(n-n^2+d^2) \sinh\left[\frac{(N_A-2i)}{kT}\Delta\epsilon\right] - d\cosh\left[\frac{(N_A-2i)}{kT}\Delta\epsilon\right]\right\} \qquad \text{(IV,6)}$$

nce $m = 2(N_A - 2i)$.

QUATION IV,6 is developed in APPENDIX II. Here, as in our first
oblem, the total flux can be expressed in polynomial form as follows:

$$\text{Total flux} = K\left[\sum_{p=0}^{p=z-1} A_p(n)\sinh\frac{p\,\Delta\epsilon}{kT} - B_p(n)\cosh\frac{p\,\Delta\epsilon}{kT}\right] \qquad \text{(IV,7)}$$

ere $A_p(n)$ and $B_p(n)$ denote polynomials in n of order of $2(z-1)$.

In spite of the apparent similarity of EQUATION IV,7 to EQUATION
,8 the polynomials involved are of entirely different form. The constant
differs from the K in EQUATION II,8. However, as it was in the previ-
s case for $\Delta\epsilon > 0$, the equation for the total flux is composed of 2
rms, the first of which describes the contragradient part of the flow
ross the boundary, while the second term describes the cogradient part
the flow. When $\Delta\epsilon < 0$, both parts are cogradients, and the total flux is
ways negative.

Numerical computations of EQUATION A II,2 (APPENDIX I) were per-
rmed on the electronic digital computer. For $\Delta\epsilon/kT$, 7 possible values
re selected at successive intervals of 0.2, covering the range of
$< \Delta\epsilon/kT \leqslant 1.4$. Negative values of $\Delta\epsilon/kT$ were not used, since then
flux will always be cogradient. When $\Delta\epsilon/kT$ exceeds 1.5, the flux is
ntragradient for almost every value of n, except for a very narrow strip
ar the "edges" ($n = 0$ and $n = 1$). Successive values of both n and d
re increased by intervals $\Delta n = 0.05$ and $\Delta d = 0.05$. Since the equation
flux remains unchanged when n and $1-n$ are interchanged, only
lues of $n \leqslant 0.5$ needed to be considered.

The results of the computations are presented in FIGURES 10 to 13.

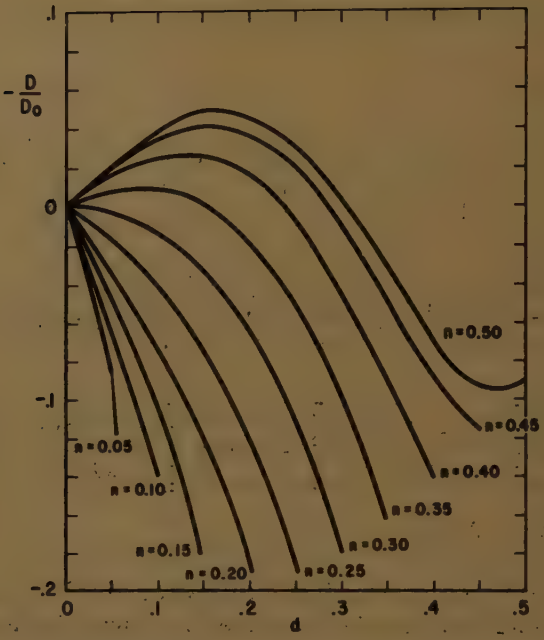

FIGURE 10. The dependence of the net flux on the concentration differenc at the interphase boundary $\Delta\epsilon/kT = 0.80$.

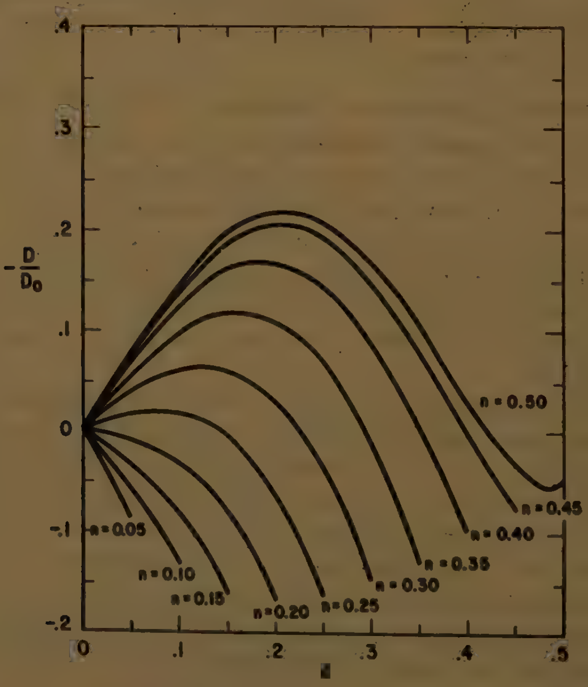

FIGURE 11. The dependence of the net flux on the concentration differenc at the interphase boundary $\Delta\epsilon/kT = 100$.

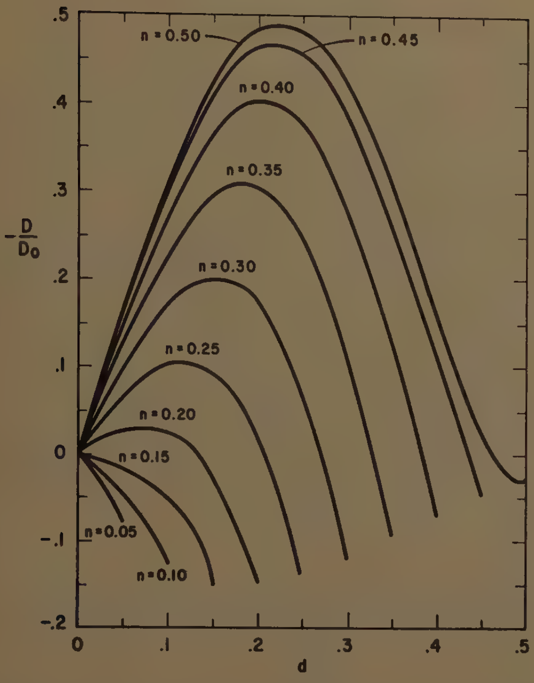

FIGURE 12. The dependence of the net flux on the concentration difference t the interphase boundary $\Delta\epsilon/kT = 1.20$.

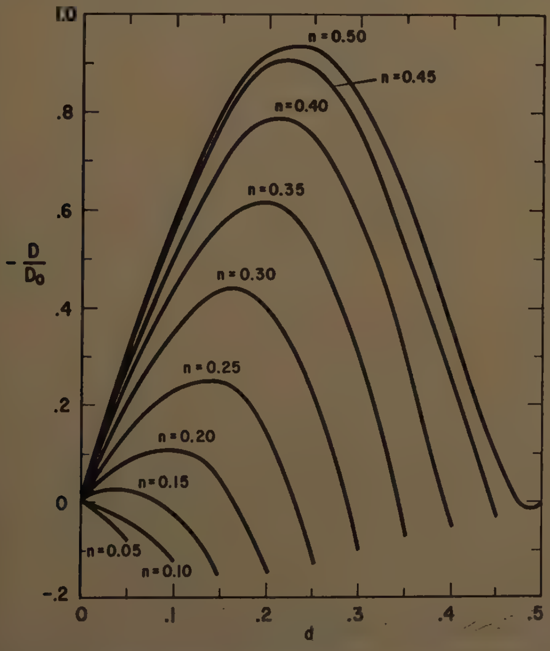

FIGURE 13. The dependence of the net flux on the concentration difference t the interphase boundary $\Delta\epsilon/kT = 1.40$.

For $\Delta\epsilon/kT < 0.8$ the net flux is always cogradient, and therefore we di not bother to plot these results. In FIGURES 10 to 13, the total flux (o more correctly, the quantity proportional to the total flux) is plotted as function of d for given values of n and $\Delta\epsilon/kT$.

The results of these computations throw light upon the problem of wha we call "metastable equilibria" between 2 liquid phases of differen concentrations. In order to be able to interpret our results in terms o phase "pseudoequilibria," it is important to examine the particular cases when the net flux is *zero* and to make use of a thermodynamic model.

TABLE 1, which is prepared from the data of FIGURES 10, 11, 12, an 13, describes the conditions for zero flux. In this table, $(n + d)$ is th concentration of phase 2 in thermodynamic equilibrium with the concentration of phase 1, which is $(n - d)$. We notice that as $(n - d)$ is plotte

TABLE 1

CONDITIONS FOR ZERO FLUX CONCENTRATION DIFFERENCE OF THE POINT OF DISCONTINUITY (= 2 D)

	$\Delta\epsilon/kT = 0.8$		= 1.0		= 1.2		= 1.4	
n	$n+d$	$n-d$	$n+a$	$n-d$	$n+d$	$n-d$	$n+d$	$n-d$
0.5	0.8025	0.1975	0.925	0.075	0.965	0.035	0.9830	0.0170
0.45	0.7325	0.1675	0.85	0.050	0.882	0.018	0.8925	0.0075
0.40	0.638	0.1620	0.75	0.050	0.782	0.018	0.7930	0.0070
0.35	0.505	0.195	0.6450	0.0550	0.680	0.020	0.6925	0.0080
0.30			0.5250	0.075	0.568	0.032	0.5880	0.0120
0.25			0.3925	0.1075	0.4575	0.0425	0.4820	0.0180
0.20					0.3325	0.0675	0.368	0.0320
0.15							0.240	0.0600
0.10								
0.05								

versus $(n + d)$ as in FIGURE 14, the curves have minima. These minim gradually move toward lower values of $(n + d)$ and higher values of $(n - d$ as $\Delta\epsilon$ approaches $\Delta\epsilon^*$. By $\Delta\epsilon^*$ we understand the smallest energy tha will still bring a contragradient flux. As $\Delta\epsilon$ approaches $\Delta\epsilon^*$, the point o zero flux will gradually move toward $n = 0.5$, $d = 0$.

The results obtained thus far conform well with the thermodynamic model discussed in PART I. The 2 phases of thermodynamic equilibrium have identical values of dF/dn. Suppose that we have phase 1, whose composition in terms of molar fraction of component A can be depicted b

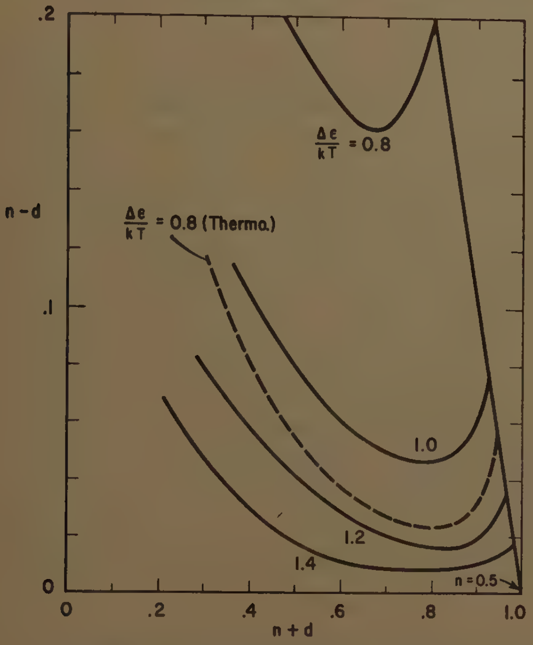

FIGURE 14. Conditions for zero net flux concentration of phase I versus centration of phase II for several values of $\Delta\epsilon/kT$.

point on an excess free-energy curve to the left of the point *A* (see GURE 15). This phase can be in an equilibrium with phase 2, of either 2 possible compositions that are located to the right and to the left of inflection point *D*. One of them will correspond to the absolutely stable configuration (the part of the curve between points *C* and *D*), d the other to the metastable configuration (between points *D* and *B*). the concentration under consideration reaches point *X*, we obtain a se where the phase under consideration can form no such equilibrium h any other configuration to the right of point *A*. It is obvious that this int *X* will correspond to the minimum value of $(n - d)$ of FIGURE 14 d TABLE 1.

This situation can be described best on the hypothetical (dF/dn) rsus *n* curve (FIGURE 16): the points *X*, *A*, *B*, *C*, and *D* are exactly same points as indicated on FIGURE 15. The part of the curve between points *C* and *D* represents absolutely unstable states. Again, we rt with point *A*. The corresponding point that represents phase 2 in an uilibrium with it is point *B*. As we move down to the left of point *A*, corresponding pseudoequilibrium concentration of phase *B* moves wn along the *BD* curve. As we reach point *X*, we reach the minimum ssible concentration of phase 1 that can be in contact with some contration corresponding to phase 2.

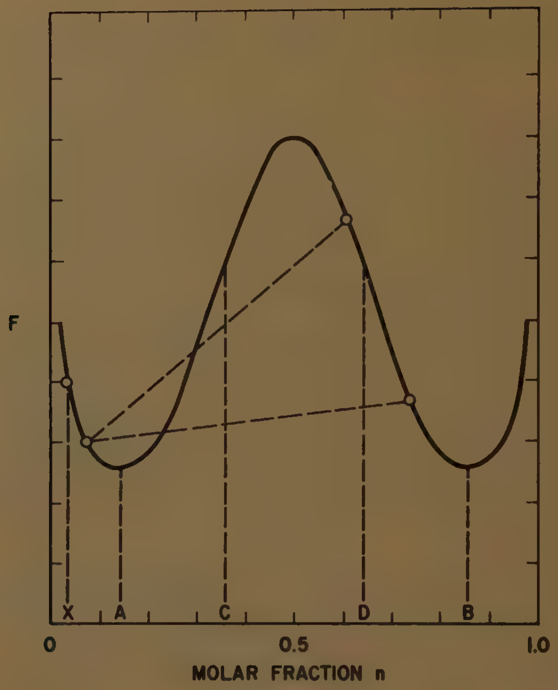

FIGURE 15. Free energy of a binary mixture. The interconnected dots indicate pseudoequilibria between 2 binary mixtures.

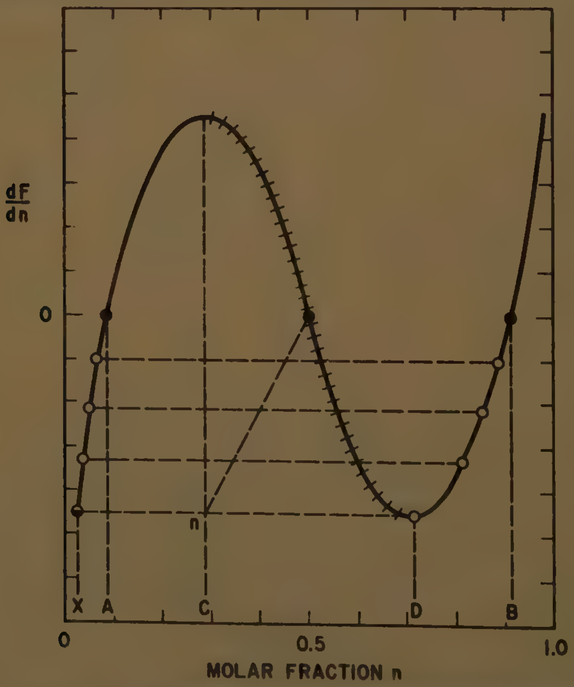

FIGURE 16. Pseudoequilibria between 2 binary mixtures.

Going back to our kinetic model, we see that each concentration of ase 1 (indicated by $[n - d]$) above a certain value corresponds to 2 val- es of concentrations of phase 2 (indicated by $[n + d]$).

Only one of these values is physically possible. These permissible ncentrations lie to the right of the minima of the $(n - d)$ versus $(n + d)$ rves (points between B and D of FIGURES 15 and 16). The concentra- ons to the left of these minima are physically impossible, since they ill fall into the absolutely unstable region between points C and D of e same figures (where either d^2F/dn_1^2 or $d^2F/dn_2^2 < 0$).

Thus far our kinetic model agrees qualitatively with the thermodynamic odel. In order to make a quantitative comparison, we calculate the free- ergy curve of binary solutions, assuming that the molecules are ran- mly distributed (the so-called "zeroth-order" approximation of Bragg d Williams). The results are given in FIGURE 17. In this figure F_1/dn_1 is plotted against n_1, for $\Delta\epsilon/kT = 0.8$. The calculations are sed upon the equation

$$\frac{dF_1}{dn_1} = \log \frac{n_1}{1 - n_1} + (1 - 2n_1)\frac{z\Delta\epsilon}{kT} \qquad \text{(IV,8)}$$

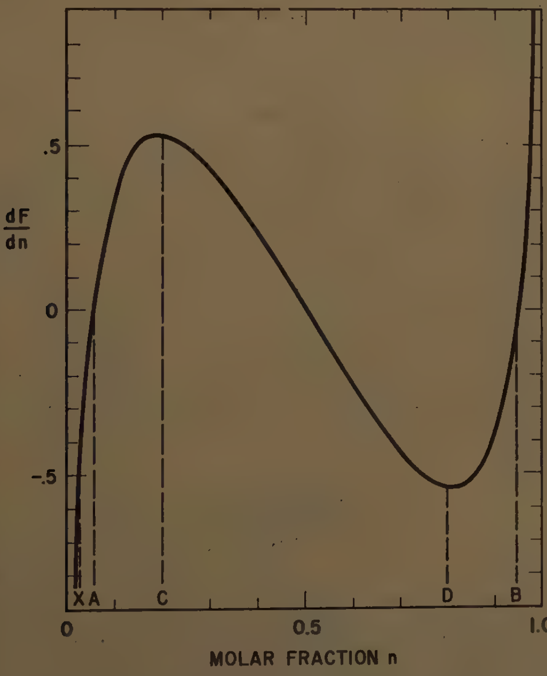

FIGURE 17. Differences in concentration (dF/dN) versus the concentration calculated according to EQUATION V,10 for $\Delta\epsilon/kT = 0.80$.

In FIGURE 17, all points of interest *(X, A, B, C, D)* are indicated in identical fashion as in FIGURES 15 and 16. From FIGURE 17 we obtain the 2 concentrations $(n - d)$ and $(n + d)$, which are in zero-flux contac (identical values of dF/dn); the results are plotted in FIGURE 14 (*broken line*). We see that the shape of the $(n - d)$ versus $(n + d)$ curves is very similar to that of the curves obtained from the kinetic model, except fo the energy factor. The results derived from EQUATION IV, 8 for $\Delta\epsilon/kT =$ 0.8 are similar to the results based upon the kinetic model with $\Delta\epsilon/kT =$ 1.15. In spite of the poor quantitative agreement, the thermodynamic and kinetic treatments lead to the same qualitative conclusion, which may be stated as follows:

It is commonplace that, when 2 saturated solutions (n_1 and n_2 of FIGURE 1) are in contact, there is a zero diffusional flux across the interfacial boundary despite the discontinuity in concentration. It would now appear possible, in principle, to observe a zero flux across the boundary between 2 solutions that are not in equilibrium if the concentrations are properly chosen. Compared with the saturated solutions (n_1 and n_2), both of these phases must be overrich in the same species. Thus, one phase will be unsaturated, the other supersaturated. If the supersaturated phase is metastable (rather than absolutely unstable), the 2-phase system as a whole would appear to be metastable.

SUMMARY

The diffusion behavior of supersaturated binary solutions is treated theoretically on the basis of a lattice model. A supersaturated solution may be either metastable or absolutely unstable. In the region of absolute instability the diffusion coefficient is negative; fluctuations in concentration are amplified by diffusion, and phase separation occurs spontaneously.

The theory also indicates the possibility of metastable 2-phase systems in which 2 solutions in contact exhibit a zero diffusional flux across the interfacial surface even though the 2 concentrations are not in thermodynamic equilibrium.

APPENDIX I

In order to calculate the total flux of component *A* to the right (the positive x axis), we multiply EQUATIONS II,7 by the number of equivalent configurations, and we then add these products for all possible arrangements of the molecules in the atmosphere. This is done as follows

Let the *i* molecules *A* be distributed among the sites at the left side o the atmosphere in such a way that j_0 of them will occupy the sites with

$= 0$, and $i - j_0$ will occupy the sites with $l = 1$. Similarly, j_2 of the maining $N_A - i$ molecules of kind A will occupy the sites with $l = 3$, d $N_A - i - j_3$ will occupy the sites with $l = 2$. Also, let a denote the mber of sites along $l = 0$ and $l = 3$, and $N/2 - a$ denote the number of tes along $l = 1$ and $l = 2$. The total number of possible arrangements of $_A$ molecules with given values of j_1 and j_2 and i among N sites is

$$g = \binom{a}{j_0}\binom{a}{j_3}\binom{\frac{N}{2} - a}{i - j_0}\binom{\frac{N}{2} - a}{N_A - i - j_3} \qquad \text{(AI,1)}$$

he energy of each possible arrangement depends always only upon 2 ariables i and N_A, since each molecule in the atmosphere forms the me bond with the central molecule, irrespective of a.

The equation for the total flux is now (from EQUATION II,7 and after troducing a new variable $p = N_A - 2i$):

$$\text{Total flux} = k\,\Delta x\,\frac{\partial n}{\partial x}\left[\sum_{N_A=0}^{N}\ \sum_{p=\frac{-N}{2}}^{\frac{N}{2}}\ \sum_{j_1=0}^{a}\ \sum_{j_3=0}^{a} g(N_A, i, j_0, j_3)\right.$$

$$n^{N_A}(1-n)^{N-N_A}\left\{(1-n)\left[\frac{N_A - p}{2} - j_0 + 2\left(\frac{N_A + p}{2} - j_3\right) + 3j_3\right] + \right.$$

$$\left.\left. n\left[\frac{N_A - p}{2} - j_0 + 2\left(\frac{N_A + p}{2} - j_3\right) + 3j_3\right]\right\} 2\sinh\frac{p\,\Delta\epsilon}{kT} - e^{p\Delta\epsilon/kT}\right]$$

(AI,2)

me terms that obviously are odd functions of p have been dropped from QUATION AI,2. In EQUATION AI,2

$$g(N_A, p, j_0, j_3) = \binom{a}{j_0}\binom{a}{j_3}\binom{\frac{N}{2} - a}{\frac{N_A - p}{2} - j_0}\binom{\frac{N}{2} - a}{\frac{N_A + p}{2} - j_3}$$

Therefore,

$$\text{Total flux} = K' \sum_{N_A=0}^{N} \sum_{p=-\frac{N}{2}}^{\frac{N}{2}} \sum_{j_0=0}^{a} \sum_{j_3=0}^{a} g\,(N_A,\, p,\, j_0,\, j_3)$$

$$n^{N_A}\,(1-n)^{N-N_A} \left\{\left[\frac{3N_A+p}{2} + j_3 - j_0\right] 2\sinh\frac{p\,\Delta\epsilon}{kT} - e^{p\Delta\epsilon/kT}\right\}$$

$$K' = K\,\Delta x\,\frac{\partial n}{\partial x} \qquad \text{(AI,3)}$$

Let us sum over positive and over negative values of p separately, in such a way that the summation over p will run from 0 to $N/2$. Then

$$\text{Total flux} = K' \left\{ \sum_{N_A=0}^{N} \sum_{p=1}^{\frac{N}{2}} \sum_{j_0=0}^{a} \sum_{j_3=0}^{a} n^{N_A}\,(1-n)^{N-N_A}\right.$$

$$\left[g\,(N_A,\, p,\, j_0,\, j_3) \left(\frac{3N_A+p}{2} + j_3 - j_0\right) - g\,(N_A,\, -p,\, j_0,\, j_3)\right.$$

$$\left.\left.\left(\frac{3N_A-p}{2} + j_3 - j_0\right) \; 2\sinh\frac{p\,\Delta\epsilon}{kT}\right\} - K' \sum_{N_A=0}^{N} \sum_{p=1}^{\frac{N}{2}} n^{N_A}\right.$$

$$\left.(1-n)^{N-N_A}\; g\,(N_A,\, p)\left(2\cosh\frac{p\,\Delta\epsilon}{kT} - 1\right)\right\} \qquad \text{(AI,4)}$$

where parts I and II are enclosed by braces ({ }). As we show below, the first part describes the contribution of the contragradient flow to the total flux, while the second part describes the contribution of the cogradient flow toward the total flow when $\Delta\epsilon > 0$. This is so since part II is inde-

dent of the arrangement of molecules inside the atmosphere. In
UATION AI,4

$$g\,(N_A\,,\,p,\,j_0\,,\,j_3) = \binom{\frac{N}{2} - a}{\frac{N_A - p}{2} - j_0}\binom{\frac{N}{2} - a}{\frac{N_A + p}{2} - j_3}\binom{a}{j_0}\binom{a}{j_3}$$

$$g\,(N_A\,,\,-p,\,j_0\,,\,j_3) = \binom{\frac{N}{2} - a}{\frac{N_A + p}{2} - j_0}\binom{\frac{N}{2} - a}{\frac{N_A - p}{2} - j_3}\binom{a}{j_0}\binom{a}{j_3}$$

$$g\,(N_A\,,\,p) = \binom{\frac{N}{2}}{\frac{N_A + p}{2}}\binom{\frac{N}{2}}{\frac{N_A - p}{2}} \qquad \text{(AI,5)}$$

now have an equation for the total flux in its final form. We will con-
er the case of $a \simeq 1$, only. After summing EQUATION AI,5 over j_0 and
we obtain the following contributions of the contragradient and co-
dient flows to the total flux:

$$= K' \sum_{N_A=0}^{N} \sum_{p=1}^{\frac{N}{2}} n^{N_A}(1-n)^{N-N_A} \left\{ p \left[\binom{\frac{N}{2} - 1}{\frac{N_A - p}{2}}\binom{\frac{N}{2} - 1}{\frac{N_A + p}{2}} + \right.\right.$$

$$\left.\binom{\frac{N}{2} - 1}{\frac{N_A - P}{2} - 1}\binom{\frac{N}{2} - 1}{\frac{N_A + p}{2} - 1}\right] + (p+2)\binom{\frac{N}{2} - 1}{\frac{N_A - p}{2} - 1}\binom{\frac{N}{2} - 1}{\frac{N_A + p}{2}} +$$

$$\left.(2-p)\binom{\frac{N}{2} - 1}{\frac{N_A - p}{2}}\binom{\frac{N}{2} - 1}{\frac{N_A + p}{2} - 1}\right\} \cdot 2 \sinh \frac{p\,\Delta\epsilon}{kT} \qquad \text{(AI,6)}$$

$$\mathrm{II} = K'\left\{ \sum_{N_A=0}^{N} \sum_{p=1}^{\frac{N}{2}} n^{N_A}(1-n)^{N-N_A} \binom{\frac{N}{2}}{\frac{N_A-p}{2}} \binom{\frac{N}{2}}{\frac{N_A+p}{2}} \right.$$

$$2\cosh\frac{p\Delta\epsilon}{kT} + \sum_{N_A=0}^{N} n^{N_A}(1-n)^{N-N_A} \binom{\frac{N}{2}}{\frac{N_A}{2}}^2 \qquad (\mathrm{AI},7)'$$

Note that when $p = 0$, $I = 0$ and $II = 1$, by binomial expansion (EQUATION AI,7).

Before summing parts I and II over p and N_A we should stress the fact that the "factorial" terms represented by symbols $\binom{a}{b}$ are composed of integers only. Therefore, N_A is an odd integer when p is an odd integer, and N_A is an even integer when p is an even integer. The final results for the total flux are:

CASE I: $z = 4$ $(N = 6)$:

$$\begin{aligned} \text{Total flux} = K'\{&n^3(1-n)^3[10\sinh 3x - 2\cosh 3x] \\ &+ [n^4(1-n)^2 + n^2(1-n)^4]\cdot[20\sinh 2x - 6\cosh 2x] \\ &- [n^5(1-n) + 3n^3(1-n)^3 + n(1-n)^5]\cdot[10\sinh x - 6\cosh x] \\ &- [n^6 + 9n^4(1-n)^2 + 9n^2(1-n)^4 + (1-n)^6]\} \end{aligned} \qquad (\mathrm{AI},8)$$

CASE II: $z = 6$ $(N = 10)$:

$$\begin{aligned} \text{Total flux} = K'\ &n^5(1-n)^5[14\sinh 5x - 2\cosh 5x] \\ &+ [n^6(1-n)^4 + n^4(1-n)^6][56\sinh 4x - 10\cosh 4x] \\ &+ [n^7(1-n)^3 + 2.5n^5(1-n)^5 + n^3(1-n)^7][84\sinh 3x - 20\cosh 3x] \\ &+ [n^8(1-n)^2 + 5n^6(1-n)^4 + 5n^4(1-n)^6 + n^2(1-n)^8] \\ &[56\sinh 2x - 20\cosh 2x] + [n^9(1-n) + 10n^7(1-n)^3 \\ &+ 20n^5(1-n)^5 + 10n^3(1-n)^7 + n(1-n)^9][14\sinh x - 10\cosh x] \\ &- [n^{10} + 25n^8(1-n)^2 + 100n^6(1-n)^4 + 100n^4(1-n)^6 \\ &+ 25n^2(1-n)^8 + (1-n)^{10} \end{aligned} \qquad (\mathrm{AI},9)$$

ASE III: $z = 8$ $(N = 14)$:

$$\text{Total flux} = K' \quad n^7 (1-n)^7 [18 \sinh 7x - 2 \cosh 7x]$$

$$+ [n^8 (1-n)^6 + n^6 (1-n)^8] [108 \sinh 6x - 14 \cosh 6x]$$

$$[n^9 (1-n)^5 + \frac{7}{3} n^7 (1- \ )^7 + n^5 (1-n)^9] [270 \sinh 5x - 42 \cosh 5x]$$

$$+ [n^{10} (1-n)^4 + 4.2 n^8 (1-n)^6 + 4.2 n^6 (1-n)^8 + n^6 (1-n)^{10}]$$

$$[360 \sinh 4x - 70 \cosh 4x] + [n^{11} (1-n)^3 + 7 n^9 (1-n)^5$$

$$12.6 n^7 (1-n)^7 + 7 n^5 (1-n)^9 + n^3 (1-n)^{11}] [270 \sinh 3x - 70 \cosh 3x]$$

$$+ [n^{12} (1-n)^2 + \frac{35}{3} n^{10} (1-n)^4 + 35 n^8 (1-n)^6 + 35 n^6 (1-n)^8$$

$$+ \frac{35}{3} n^4 (1-n)^{10} + n^2 (1-n)^{12}] \cdot [108 \sinh 2x - 42 \cosh 2x]$$

$$+ [n^{13} (1-n) + 21 n^{11} (1-n)^3 \ 105 n^9 (1-n)^5 + 175 n^7 (1-n)^7$$

$$+ 105 n^5 (1-n)^9 + 21 n^3 (1-n)^{11} + n (1-n)^{13}]$$

$$[18 \sinh x - 14 \cosh x] - [n^{14} + 49 n^{12} (1-n)^2 + 441 n^{10} (1-n)^4$$

$$+ 1225 n^8 (1-n)^6 \ 1225 n^6 (1-n)^8 + 441 n^4 (1-n)^{10}$$

$$+ 49 n^2 (1-n)^{12} + (1-n)^{14}] \qquad \text{(AI,10)}$$

all these equations $x = \Delta\epsilon/kT$.

APPENDIX II

We rewrite EQUATION IV,6 by introducing a new variable $p = N_A - 2i$.
hen

$$\text{Total flux} = 2K \left[(1-n)^2 - d^2 \right]^{\frac{N}{2}} \sum_{N_A=0}^{N} \sum_{p=-\frac{N}{2}}^{\frac{N}{2}} \binom{\frac{N}{2}}{\frac{N_A - p}{2}} \binom{\frac{N}{2}}{\frac{N_A + p}{2}} \left(\frac{n-d}{1-n+d} \right)^{\frac{N_A - p}{2}} \left(\frac{n+d}{1-n-d} \right)^{\frac{N_A + p}{2}}$$

$$\left[(n - n^2 + d^2) \sinh \frac{p\Delta\epsilon}{kT} - d \cosh \frac{p\Delta\epsilon}{kT} \right] \qquad \text{(AII,1)}$$

The restrictions on p and N_A are:

$$\frac{-N}{2} \leqslant p \leqslant \frac{N}{2}; \qquad 0 \leqslant N_A \leqslant N$$

Here again, both p and N_A can be only odd integers or even integer simultaneously. In order to make EQUATION 1 more compact, the follow ing abbreviations are introduced:

$$\alpha = \frac{n+d}{1-n-d} \qquad \beta = \frac{n-d}{1-n+d}$$

Then for the specific case of $N = 6$ we obtain

$$\text{Total flux} = 2K\,[(1-n)^2 - d^2]^3 \left\{(n - n^2 + d^2)\left[(\alpha^3 - \beta^3)\sinh\frac{3\Delta\epsilon}{kT}\right.\right.$$

$$+\,3(\alpha^2 - \beta^2)(1 + \alpha\beta)\sinh\frac{2\Delta\epsilon}{kT} + 3(\alpha - \beta)(1 + 3\alpha\beta + \alpha^2\beta^2)\sinh\frac{\Delta\epsilon}{kT}$$

$$-\,d\left[(\alpha^3 + \beta^3)\cosh\frac{3\Delta\epsilon}{kT} + 3(\alpha^2 + \beta^2)(1 + \alpha\beta)\right. \qquad \text{(AII,2)}$$

$$\cosh\frac{2\Delta\epsilon}{kT} + 3(\alpha\ 0\ \beta)(1 + 3\alpha\beta + \alpha^2\beta^2)\cosh\frac{\Delta\epsilon}{kT}$$

$$\left.\left.+\,(1 + 9\alpha\beta + 9\alpha^2\beta^2 + \alpha^3\beta^3)\right]\right\}$$

For $n = 0.5$, $\alpha\beta = 1$, and we obtain

$$\text{Total flux} = 2K\,(0.5 - d)^3 \left\{(0.25 + d^2)\left[(\alpha^3 - \beta^3)\sinh\frac{3\Delta\epsilon}{kT}\right.\right.$$

$$\left.+\,6(\alpha^2 - \beta^2)\sinh\frac{2\Delta\epsilon}{kT}\ 15(\alpha - \beta)\sinh\frac{\Delta\epsilon}{kT}\right]$$

$$-\,d\left[(\alpha^3 + \beta^3)\cosh\frac{3\Delta\epsilon}{kT} + 6(\alpha^2 + \beta^2)\cosh\frac{2\Delta\epsilon}{kT}\right.$$

$$\left.\left.+\,14(\alpha\ 0\ \beta)\cosh\frac{\Delta\epsilon}{kT} + 20\right]\right\} \qquad \text{(AII,}$$

In the limiting case of $\Delta\epsilon = 0$ we have

$$\text{Total flux} = -2Kd \qquad \text{(AII,4)}$$

nce $(1 - n)^2 - d^2 = (1\ 0\ \alpha)\ (1\ 0\ \beta)$ and from binomial expansion of QUATION AII,2. For the case in which pure solutions are in contact, $= d$, and we have

$$\text{Total flux} = -2K\, n\left[1 - 2n\,(1 - e^{-\Delta\epsilon/kT})\right]^{N/2} < 0 \qquad \text{(AII,5)}$$

For $n = 0.5$ and $n = d$ we have

$$\text{Total flux} = -Ke^{-N\Delta\epsilon/kT} \qquad \text{(AII,6)}$$

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